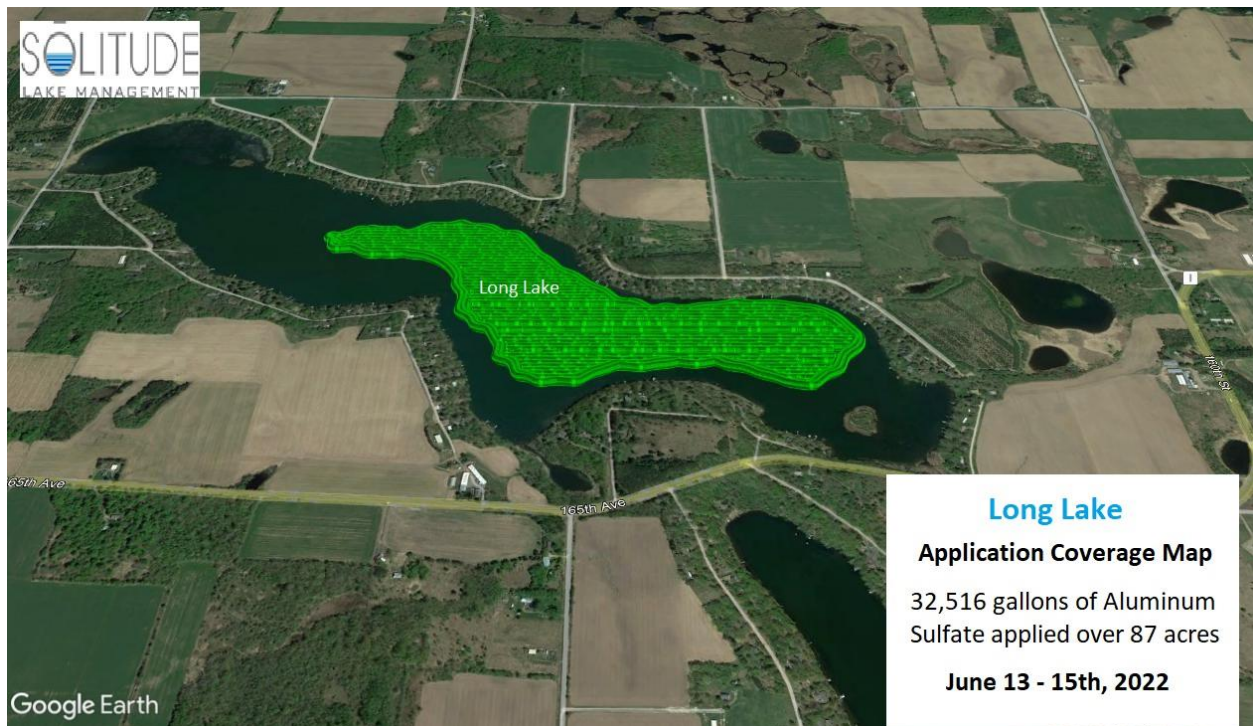


Long Lake, Wisconsin - Limnological response to alum treatment: 2022 interim report

1 January 2023



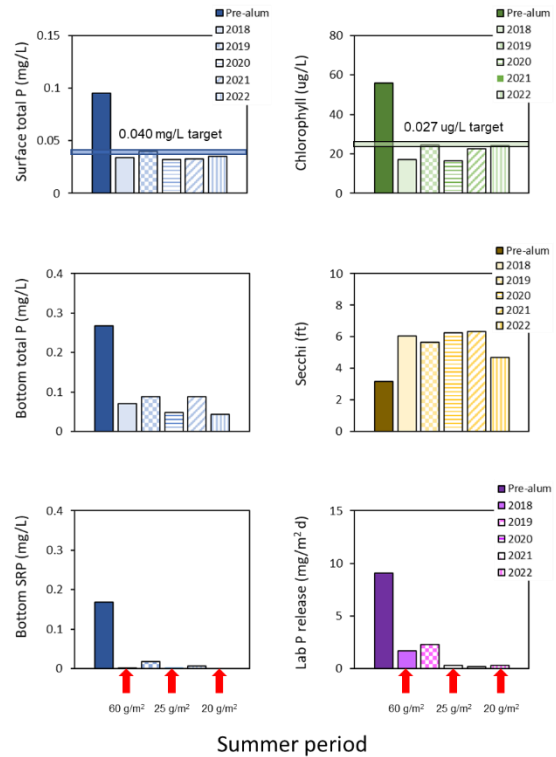
Alum application area in 2022 (SOLitude Lake Management)



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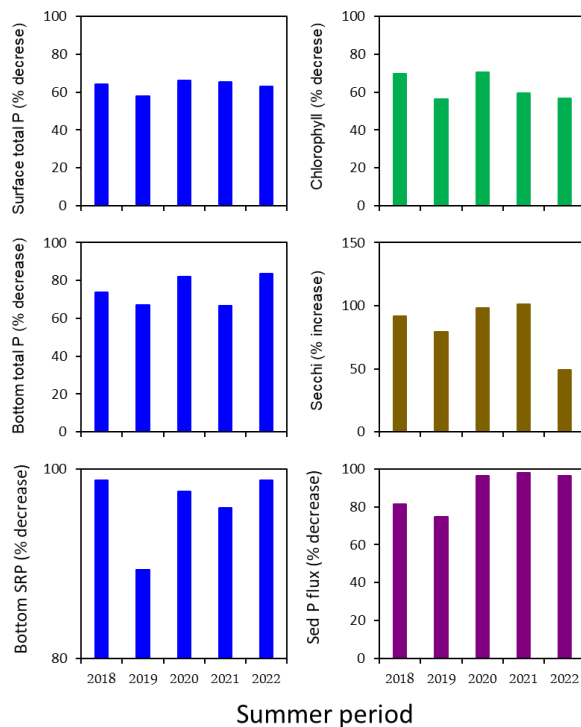
Executive summary

1. During the summer of 2022 and the 3rd alum treatment (i.e., 20 g/m² application in June 2022), mean (July-September) surface total P was 0.035 mg/L (63% reduction over the pre-treatment average), mean bottom total P and SRP were only 0.044 mg/L (83% reduction) and not detectable (99% reduction), respectively, mean chlorophyll was 24.1 µg/L (57% reduction), and mean Secchi transparency was 4.7 ft (~34% improvement) in 2022.



2. Laboratory-derived diffusive P flux from sediment under anaerobic conditions at station 30 was only 0.3 mg/m² d in September 2022, representing a 96% decline over pretreatment means. In contrast, anaerobic diffusive P fluxes before the alum treatment were much higher at 12.9 mg/m² d in 2014.

3. While WQ improvements generally continued as of 2022, the lower Secchi transparency was an anomaly. While not precisely known, the poorer water clarity in 2022 relative to other post alum treatment summers may have been due to a possible change in algal species assemblage to colonial, clump-forming algae. These types of colonies tend to cause greater light attenuation compared to filamentous algae, resulting in lower water clarity.



Objective

Shallow Long Lake (273 ac surface area) has exhibited excessive summer cyanobacterial blooms and poor water quality (WQ) conditions (high phosphorus and chlorophyll concentrations and low water clarity) linked to internal phosphorus (P) recycling from sediments (James & Clemens 2017). A total aluminum sulfate (alum) dosage of $\sim 105 \text{ g/m}^2$ split into lower concentrations and spread out over 2-year intervals was recommended to control internal P loading. The first alum dosage of 60 g/m^2 was applied to sediments located within the 15-ft depth contour of the lake on 11-13 June 2018 (HAB Aquatic Solutions). The second and third alum applications of $\sim 25 \text{ g/m}^2$ and 20 g/m^2 , respectively, were applied over the same depth contour in 2020 and 2022.

Post-treatment monitoring of water and sediment chemistry was started in 2018 to document the trajectory of water quality improvement during rehabilitation as part of a comprehensive adaptive management program aimed toward making informed decisions regarding adjusting alum application and dosage to meet future water quality goals. Post-treatment monitoring included field and laboratory research to document changes in 1) lake limnological response variables (total P, soluble reactive P, chlorophyll, Secchi transparency), 2) diffusive P flux from sediment under anaerobic conditions for stations located within and outside the treatment area, and 3) binding of P by the alum floc. Overall, lake water quality was predicted to respond to internal phosphorus loading reduction with lower total phosphorus and chlorophyll concentrations, lower bloom frequency of nuisance chlorophyll levels, and higher water transparency. The objectives of this interim report are to describe Long Lake limnological and sediment internal P loading response to alum treatment during the summer of 2022. The third alum treatment at a dose of $\sim 20 \text{ g/m}^2$ was applied to Long Lake between 13-15 June 2022.

Methods

Lake monitoring

A station located in the central, deepest area of the lake was sampled biweekly between May and September 2022 (Fig. 1). An integrated sample was collected over the upper 2-m for analysis of

total P, soluble reactive P (SRP), and chlorophyll. Additional discrete samples were collected at 1-m intervals from the lake surface to within 0.5 m of the sediment surface for analysis of these same variables. Total P samples were predigested with potassium persulfate according to APHA (2011). Total and soluble reactive P (i.e., P available for uptake by algae) were analyzed colorimetrically using the ascorbic acid method (APHA 2011). Samples for viable chlorophyll (i.e., a surrogate measure of algal biomass) were filtered onto glass fiber filters (Gelman A/E; 2.0 μ nominal pore size) and extracted in 90% acetone before fluorometric determination (EPA 445.0). Secchi transparency and in situ measurements (temperature, dissolved oxygen, pH, and conductivity) were collected on each date using a YSI 6600 sonde (Yellow Springs Instruments) that was calibrated against dissolved oxygen Winkler titrations (APHA 2011) and known buffer solutions. Vertical in situ profiles were collected at 0.5-m to 1-m intervals.

Sediment chemistry

Sediment sampling stations. Sediment cores were collected at 4 stations (10, 20, 30, and 40) in Long Lake in September 2022 (Fig. 1). These station locations coincided with those visited in 2014 (James (2014)). Station 20, 30, and 40 were located within the Al treatment zone (i.e., the 15-ft contour) while station 10 was located at a shallower depth outside the treatment zone.

Vertical variations. A sediment core was collected in September 2022 at station 30 for determination of vertical profiles of various sediment characteristics and P fractions (see Analytical methods below). Sediment cores were sectioned at 1-cm intervals between 0 and 6 cm and at 2-cm intervals below the 10-cm depth for determination of moisture content, wet and dry bulk density, loss-on-ignition organic matter, loosely-bound P, iron-bound P, labile organic P, and aluminum-bound P.

Laboratory-derived diffusive phosphorus flux from sediments under anaerobic conditions.

Anaerobic diffusive P fluxes were measured from intact sediment cores collected at all sediment sampling stations shown in Figure 1 in July 2021. Duplicate sediment cores were collected at stations 10, 20, and 40, while triplicate cores were collected at station 30, to monitor alum treatment effectiveness after the third Al application. The sediment incubation systems were

placed in a darkened environmental chamber and incubated at 20 °C for up to 7 days. The incubation temperature was set to a standard temperature for all stations for comparative purposes. The oxidation-reduction environment in each system was controlled by gently bubbling nitrogen-CO₂ through an air stone placed just above the sediment surface to maintain anaerobic conditions.

Water samples for SRP were collected from the center of each system using a 60-cc syringe and filtered through a 0.45 µm membrane syringe filter (Nalge). The water volume removed from each system during sampling was replaced by addition of filtered lake water preadjusted to the proper oxidation-reduction condition. These volumes were accurately measured for determination of dilution effects. Rates of P release from the sediment (mg/m² d) were calculated as the linear change in mass in the overlying water divided by time (days) and the area (m²) of the incubation core liner. Regression analysis was used to estimate rates over the linear portion of the data.

Analytical methods. A known volume of sediment was dried at 105 °C for determination of moisture content, wet and dry bulk density, and burned at 550 °C for determination of loss-on-ignition organic matter content (Avnimelech et al. 2001, Håkanson and Jansson 2002).

Phosphorus fractionation was conducted according to Hietjes and Lijklema (1980), Psenner and Puckso (1988), and Nürnberg (1988) for the determination of ammonium-chloride-extractable P (loosely-bound P), bicarbonate-dithionite-extractable P (i.e., iron-bound P), and sodium hydroxide-extractable P (i.e., aluminum-bound P). Additional sediment was dried to a constant weight, ground, and digested for analysis of total Al at the University of Minnesota, Research Analytical Laboratory.

The loosely-bound and iron-bound P fractions are readily mobilized at the sediment-water interface as a result of anaerobic conditions that lead to desorption of P from sediment and diffusion into the overlying water column (Mortimer 1971, Boström 1984, Nürnberg 1988). The sum of the loosely-bound and iron-bound P fraction represents redox-sensitive P (i.e., the P fraction that is active in P release under anaerobic and reducing conditions) and will be referred to as *redox P*. Aluminum-bound P reflects P bound to the Al floc after aluminum sulfate

application and its chemical transformation to aluminum hydroxide ($\text{Al}(\text{OH})_3$).

Summary of Results

Lake limnological response

Local precipitation (measured at Amery and Luck WI) more than 0.5 inches occurred in March and April through Early June (Fig. 2). There were differences in daily precipitation between the Luck and Amery monitoring stations, particularly in early May. A series of storms with precipitation > 0.5 inches occurred in Mid-June. Daily precipitation declined in Late June through July, then another series of storms occurred in August that resulted in precipitation > 1 inch. Storm-related precipitation subsided in September. Monthly precipitation at Amery in 2022 was below the long-term average in May, June, and July, and nearly 2X above average in August, suggesting droughty conditions followed by substantial rain (Fig. 3). September 2022 monthly precipitation was also below the long-term average. (Fig. 3).

The lake briefly stratified in early June 2022 with the development of anoxia (Fig. 4). The lake turned over and mixed in late June, after the alum application period. Stratification redeveloped and was strong between July and late August (Fig. 4). Bottom anoxia developed in late June and persisted until late August. Fall turnover and reoxygenation occurred in late August 2022.

Total P and SRP concentrations were very low in the bottom waters in conjunction with the 2022 alum treatment despite hypolimnetic anoxia (Fig. 5). Bottom SRP concentrations were below detection limits throughout the summer (Fig. 5). Vertically in the water column, total P concentrations were relatively uniform throughout the stratified period (Fig. 6). Hypolimnetic total P exhibited a very minor peak above the sediment-water interface in July but concentrations were < 0.06 mg/L (Fig. 6) and bottom SRP was below detection limits, suggesting minimal internal P loading (Fig. 7).

Surface total P concentrations were low (< 0.030 mg/L) between May and early July 2022 (Fig. 8). Concentrations increased slightly and fluctuated between 0.035 mg/L and 0.039 mg/L

between late July and early September. The highest surface total P concentration was only 0.043 mg/L and occurred in late September 2022.

Although surface chlorophyll concentrations were very low in May 2022, a minor concentration peak of 23 µg/L developed in early June (Fig. 9). The surface concentration declined to < 20 µg/L in early July, then increased and fluctuated between 20 and 31 µg/L between late July and September (Fig. 9). Vertically in the water column minor chlorophyll peaks were observed in mid-June and mid-September 2022 (Fig. 6).

Secchi transparency trends were unusual in that they fluctuated between 1.1 m and 2 m throughout the growing season (Fig. 10). Unlike other years, there did not appear to be a clearing period of high transparency in May 2022. Although chlorophyll-Secchi transparency relationships were generally related in 2022 (Fig. 11), lower chlorophyll concentrations in May did not coincide with relatively higher Secchi depth, suggesting algal species assemblage might have been a bit different and perhaps dominated by colonial cells versus filaments. The former type would tend to disperse and attenuate underwater light more rapidly with depth, resulting in lower transparency.

Strong linear relationships continued to exist between 2-m integrated total P and chlorophyll over the 2017-22 summer periods, indicating algal productivity was P-limited in Long Lake and responded to lower internal P loading (Fig. 11). Secchi transparency was also inversely related to 2-m integrated chlorophyll concentrations over the 5-year summer period, suggesting that P-limited algal growth and reduction in biomass as a result of the 2018, 2020, and 2022 alum applications translated into overall greater summer water clarity in Long Lake.

A comparison of mean summer (July-September) limnological response variables before (i.e.,

Table 1. Summary of changes in lake water quality and laboratory-derived phosphorus release from sediment in Long Lake after the initial alum treatments in June 2018, 2020, and 2022. Overall goals after completion of the treatment schedule are shown in the last column. Average pre Al (i.e., limnological conditions before the start of alum treatments) represents the mean of years 2012 and 2017.

Variable		Historical (1993, 1996, 2001, 2014)	2012	2017	Average pre Al	2018 (alum)	2019	2020 (alum)	2021	2022 (alum)	Percent improvement (Pre Al versus 2022)	Goal after internal P loading control	
Lake	Mean (Jul-Sep)	Mean surface TP (mg/L)	0.092	0.129	0.061	0.094	0.034	0.040	0.032	0.033	0.035	63% reduction	< 0.040
		Mean bottom TP (mg/L)		0.150	0.386	0.268	0.040	0.088	0.048	0.089	0.044	83% reduction	< 0.050
		Mean bottom SRP (mg/L)		0.031	0.307	0.169	0.003	0.018	0.004	0.007	0.002	99% reduction	< 0.050
		Mean chlorophyll (µg/L)	53.59	69.04	43.06	55.23	17.05	24.52	16.45	22.7	24.1	57% reduction	< 20
		Mean Secchi transparency (ft)	4.17	2.43	3.87	3.49	6.04	5.65	6.23	6.33	4.69	34% increase	>10
Sediment	Station 30		Sediment diffusive P flux (mg/m ² d)	12.9	5.24	9.07	1.68	2.28	0.32	0.20	0.33	96% reduction	< 1.5

2012 and 2017) and after (i.e., 2018-22) alum treatments is shown in Figure 12. Mean bottom concentrations of total P and SRP remained very low in 2022 as a result of alum treatments (Fig. 12), representing an 83% and 99% reduction over the pretreatment mean (Table 1 and Fig. 13). Mean summer surface total P and chlorophyll improvement continued in 2022 and mean concentrations were lower by 63% and 57%, respectively (Table 1). However, mean Secchi transparency was only 34% improved in 2022 versus the pretreatment mean (Table 1). As mentioned above, algal species assemblage may have been different in 2022 (i.e., colonial cells that clump versus filaments that allow for more light penetration), resulting in overall lower water clarity in 2022.

Changes in anaerobic diffusive phosphorus flux and sediment chemistry

Laboratory-derived anaerobic diffusive P fluxes remained low at stations located in the treatment area (i.e., station 20, 30, and 40) as of September 2022 (Fig. 14). Diffusive P flux at station 30, measured in the laboratory, was very low in 2022, reflecting negligible accumulation of hypolimnetic P in the lake (Table 1).

Comparisons of vertical variations in sediment moisture content at station 30 before (June 2018) and after (September 2022) the 3 Al applications implied that the alum floc located on the sediment surface (Fig. 15). Moisture content in the upper 3-cm sediment layer exceeded 95% in September 2022, which was higher than the moisture content of the surface sediment in June 2018, immediately prior to the first Al application. This high moisture content pattern reflected the very low density (mass) of the Al floc layer in relation to the denser original sediment.

<Insert Al results here – Fig 16 and 17>

Vertically in the sediment column at station 30, Al-bound P (i.e., P bound onto the alum) concentrations were lower in the Al floc layer compared to 2021 (Fig. 18). This pattern may indicate that the Al floc has perhaps become redistributed due to lake mixing and some resuspension. However, Diffusive P flux from sediment under anaerobic conditions remained very low at this station, indicating the Al applications are very effective in controlling internal P loading.

Summary and recommendations

The 2018, 2020, and 2022 alum applications have continued to be successful in substantially reducing concentrations of total and soluble P in the hypolimnion of Long Lake as of 2022. Mean summer (July-September) bottom total P (0.044mg/L) and SRP (below detection) remained improved (i.e., reduced) by 83% and 99%, respectively, in 2022 compared to pretreatment averages. Mean surface total P was 0.035 mg/L in 2022, representing a 63% reduction in conjunction with alum treatment. The 2022 mean summer total P concentration was also below the WI state standard of 0.040 mg/L for shallow lakes (WisCALM 2019). Mean summer chlorophyll was only 24 µg/L in 2021, representing a 57% improvement over the pretreatment average. The 2022 mean also fell well below the WisCALM (2019) benchmark of 27 µg/L for aquatic habitat. Unfortunately, mean summer Secchi transparency declined to ~ 4.7 ft in 2022. This mean represented only a 34% improvement over the pretreatment average. Reasons for this discrepancy may be related to a possible change in algal species assemblage to more colonial, clump-forming cyanobacteria.

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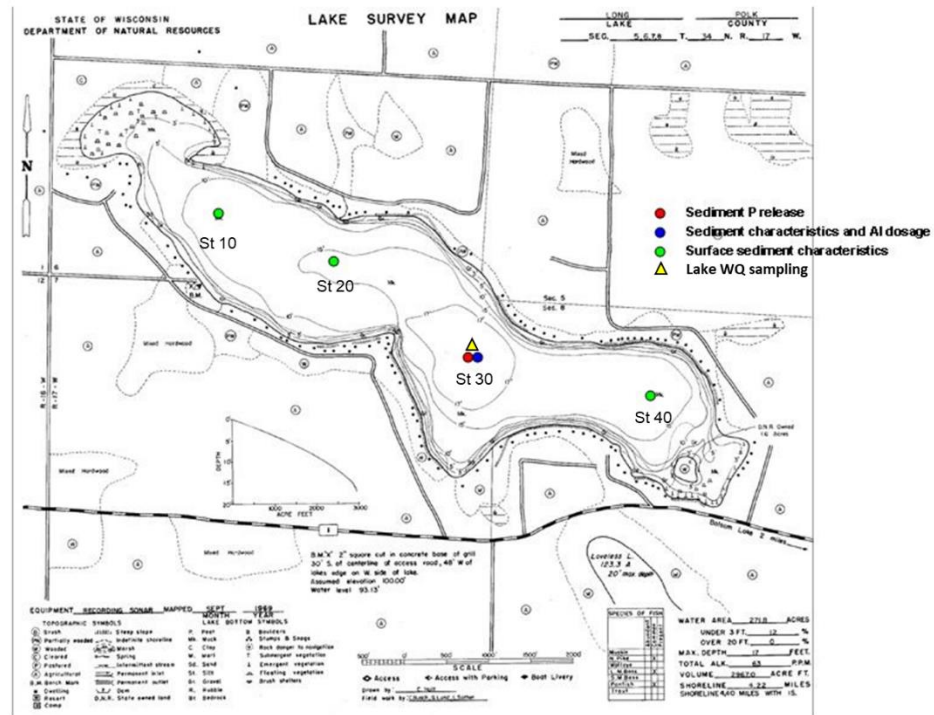


Figure 1. Sediment and water sampling stations.

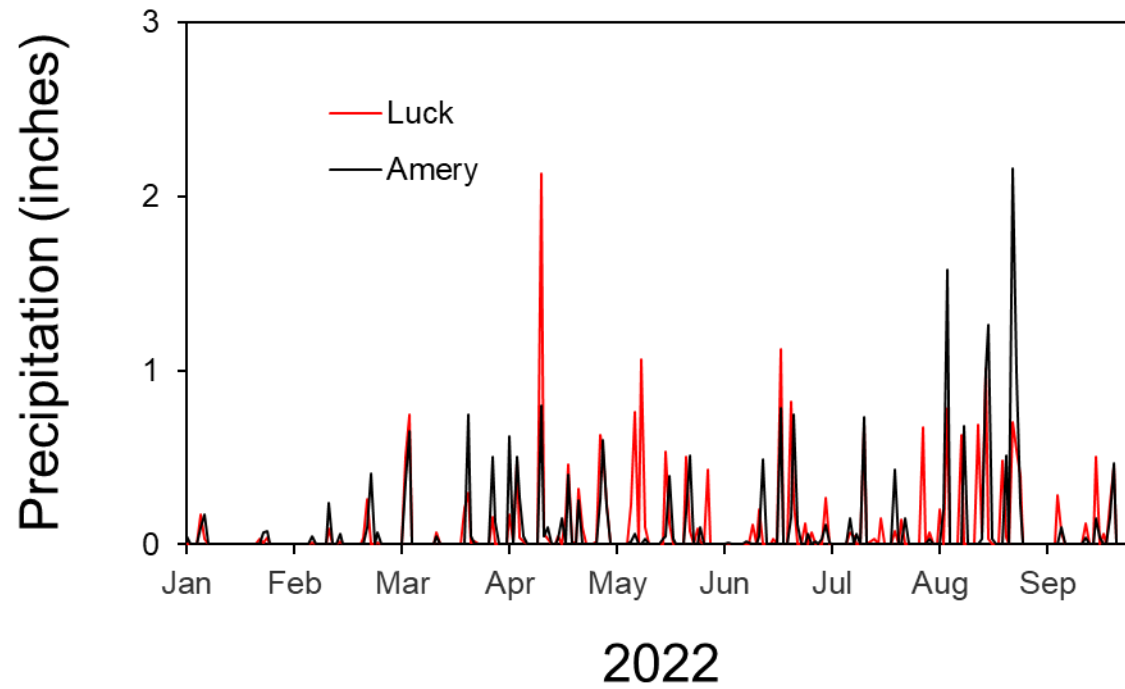


Figure 2. Variations in daily local precipitation measured at Amery and Luck WI in 2022.

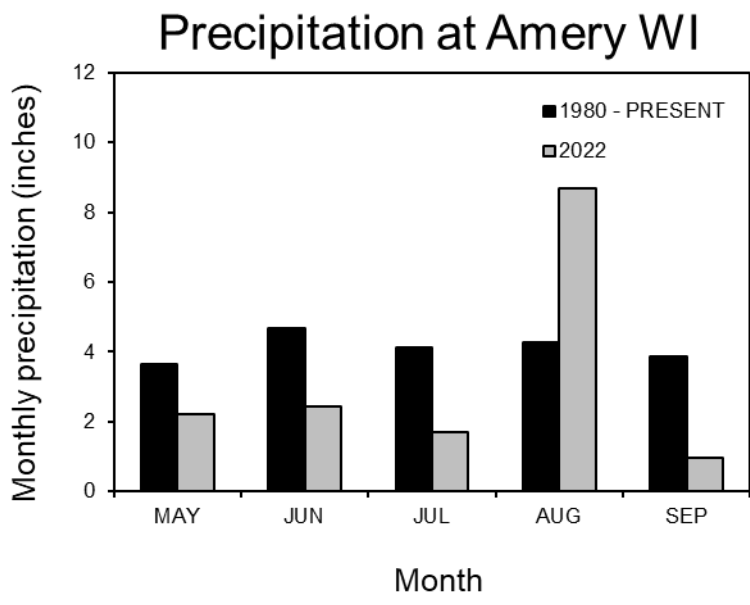


Figure 3. A comparison of average monthly precipitation (data from Amery WI).

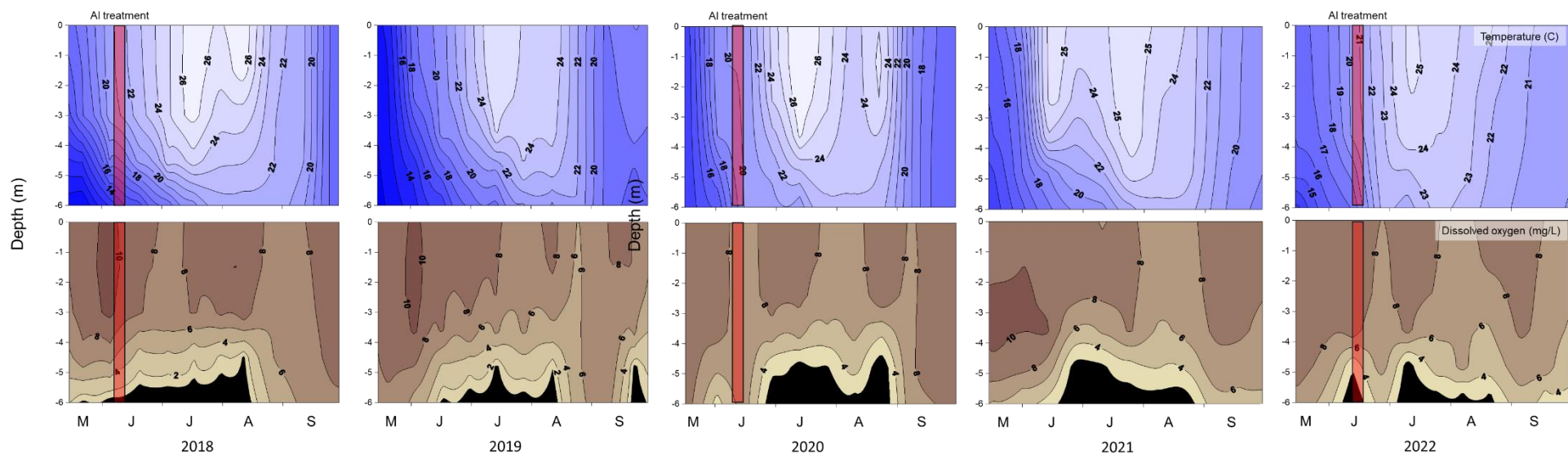


Figure 4. Seasonal and vertical variations in temperature (upper panel) and dissolved oxygen (lower panel) in 2018 -2022.

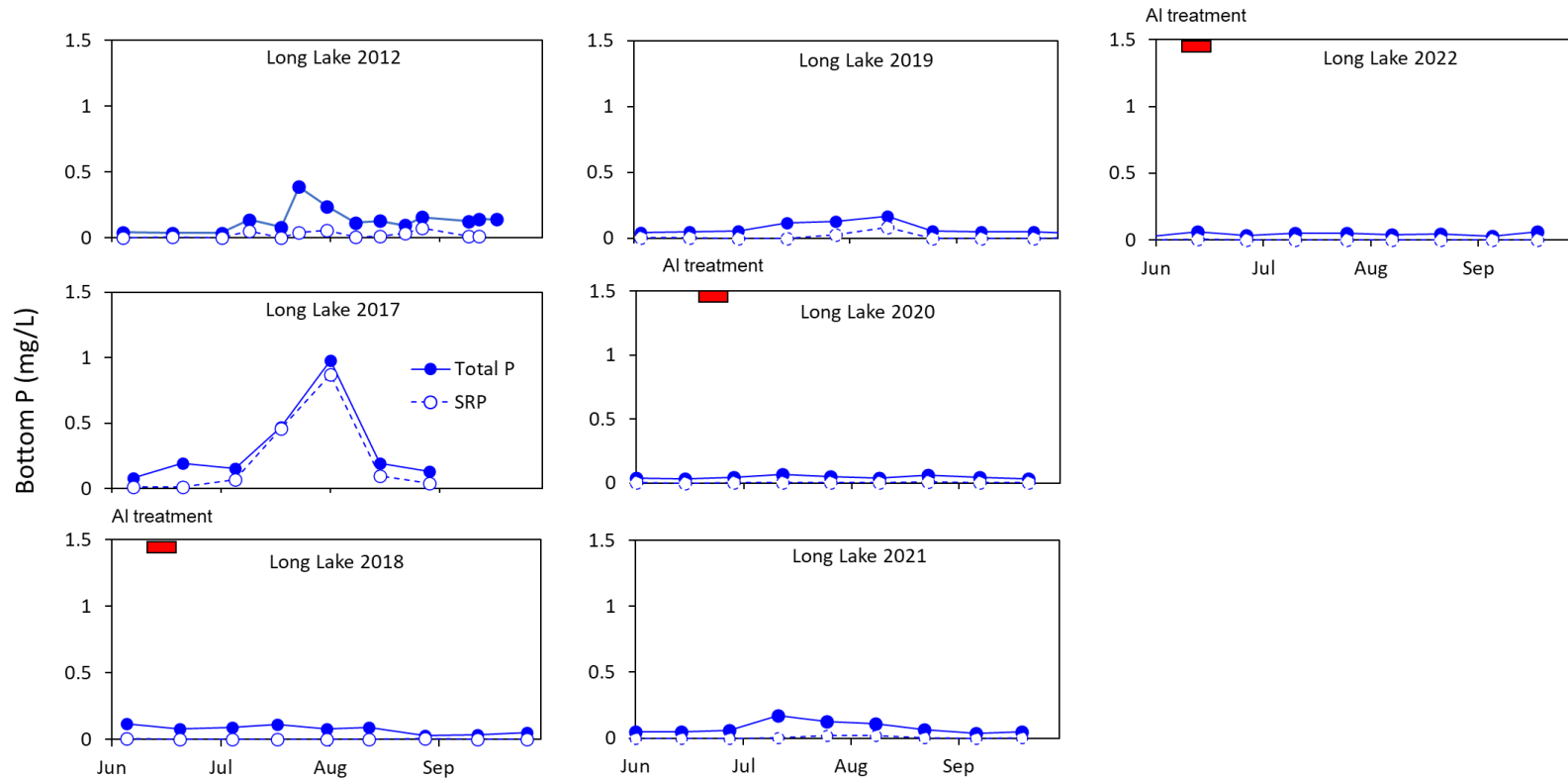


Figure 5. Seasonal variations in bottom (i.e., ~ 0.25 m above the sediment-water interface) total P, and bottom soluble reactive P (SRP) during pretreatment (2012 & 2017) and post-treatment years. Red horizontal bars denote the periods of alum treatment.

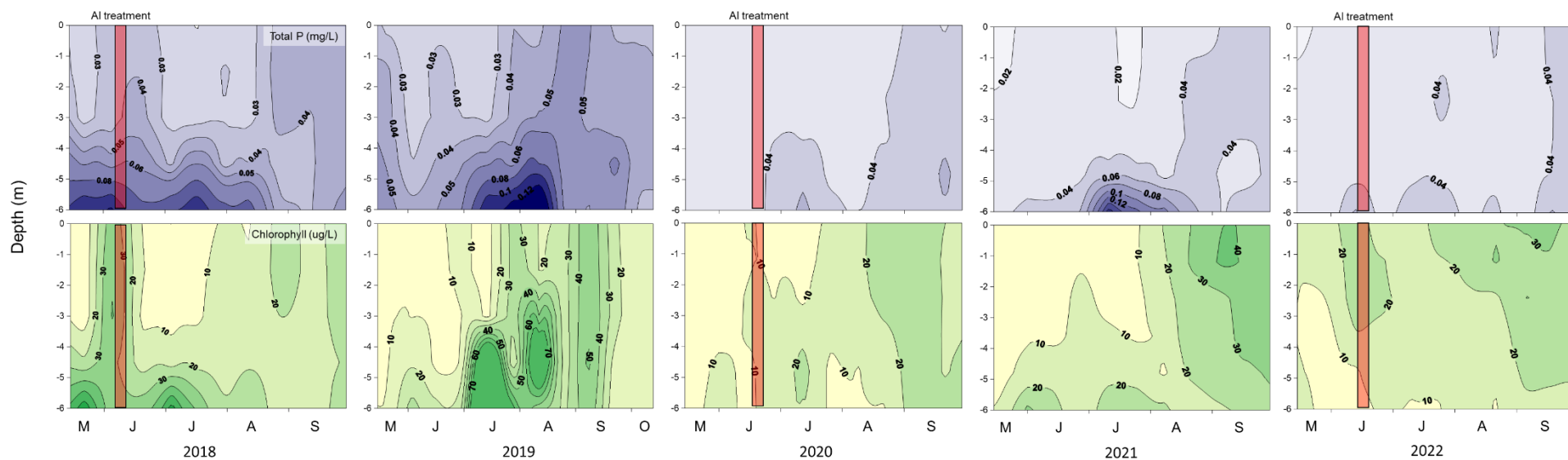


Figure 6. Seasonal and vertical variations in total phosphorus (P, upper panel) and chlorophyll (lower panel). Red horizontal bars denote periods of alum treatment.

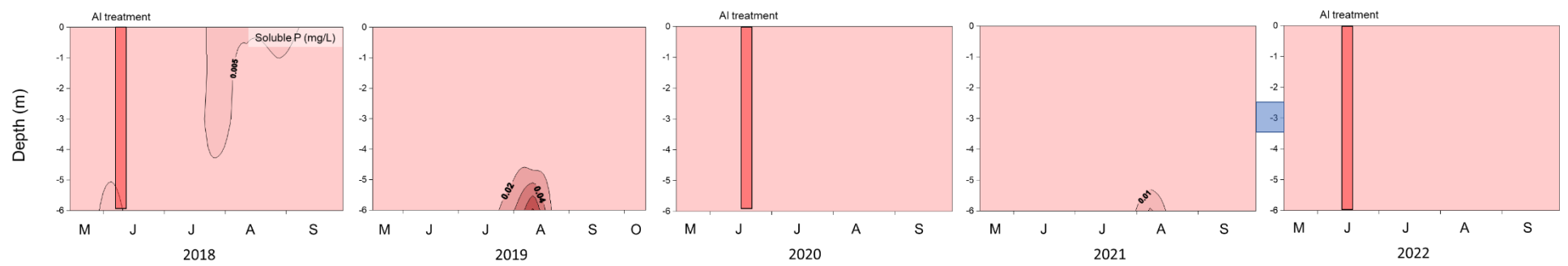


Figure 7. Seasonal and vertical variations in soluble phosphorus (SRP). Red horizontal bars denote periods of alum treatment. SRP was generally not detected in 2020 and 2022.

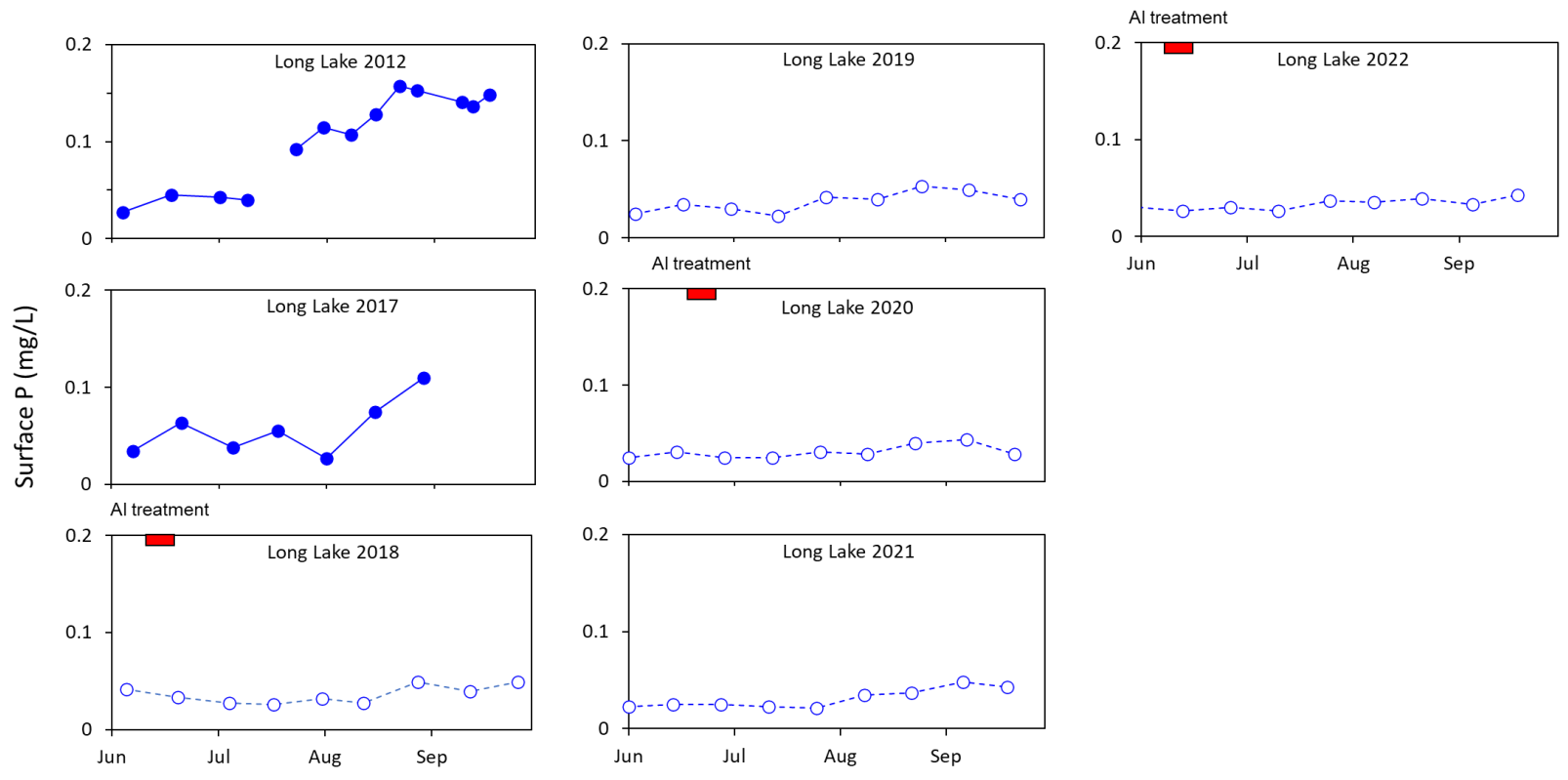


Figure 8. Seasonal variations in surface total P during pretreatment (2012 & 2017) and post-treatment years. Red horizontal bars denote the periods of alum treatment.

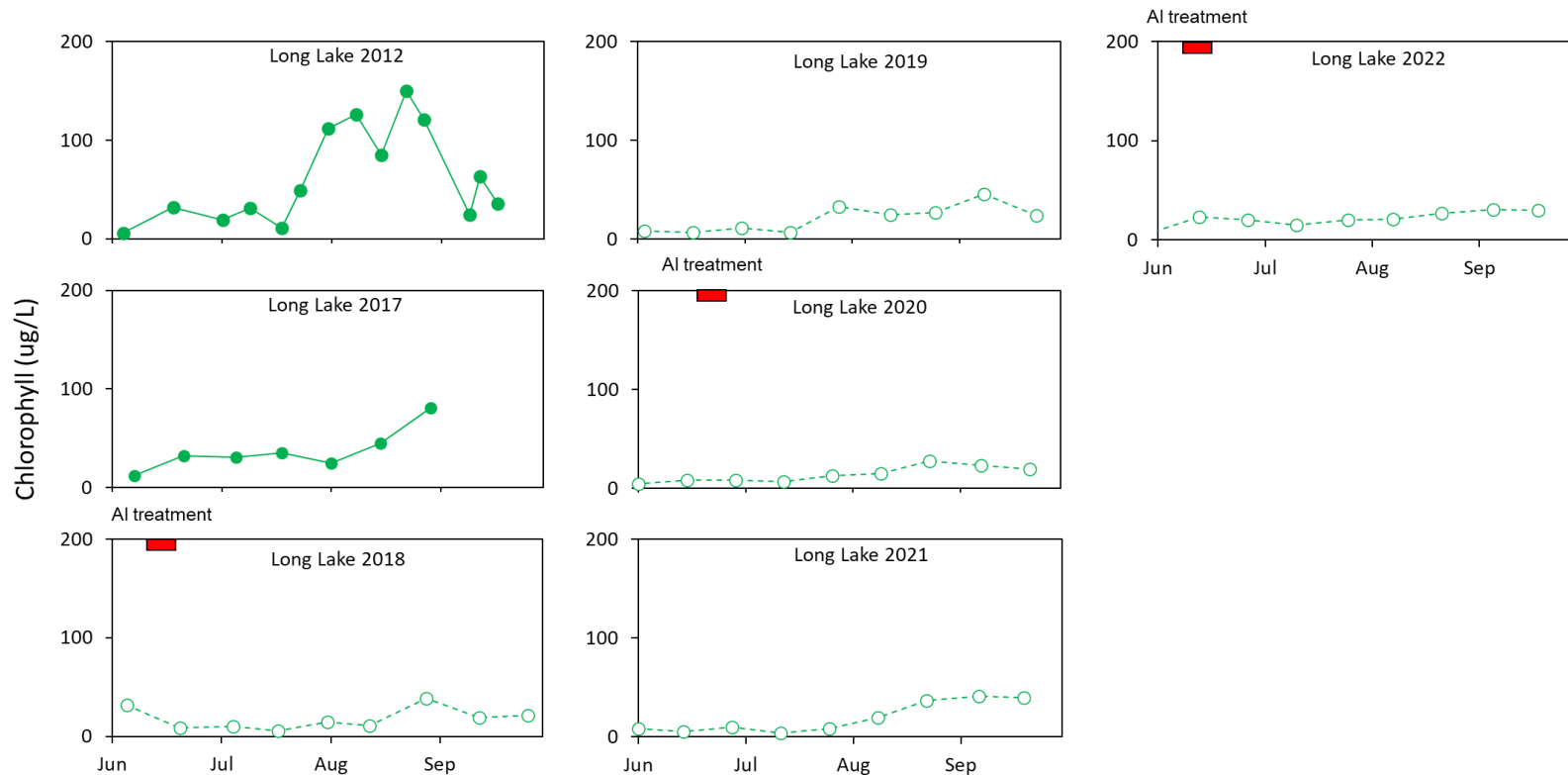


Figure 9. Seasonal variations in surface chlorophyll P during pretreatment (2012 & 2017) and post-treatment years. Red horizontal bars denote the periods of alum treatment.

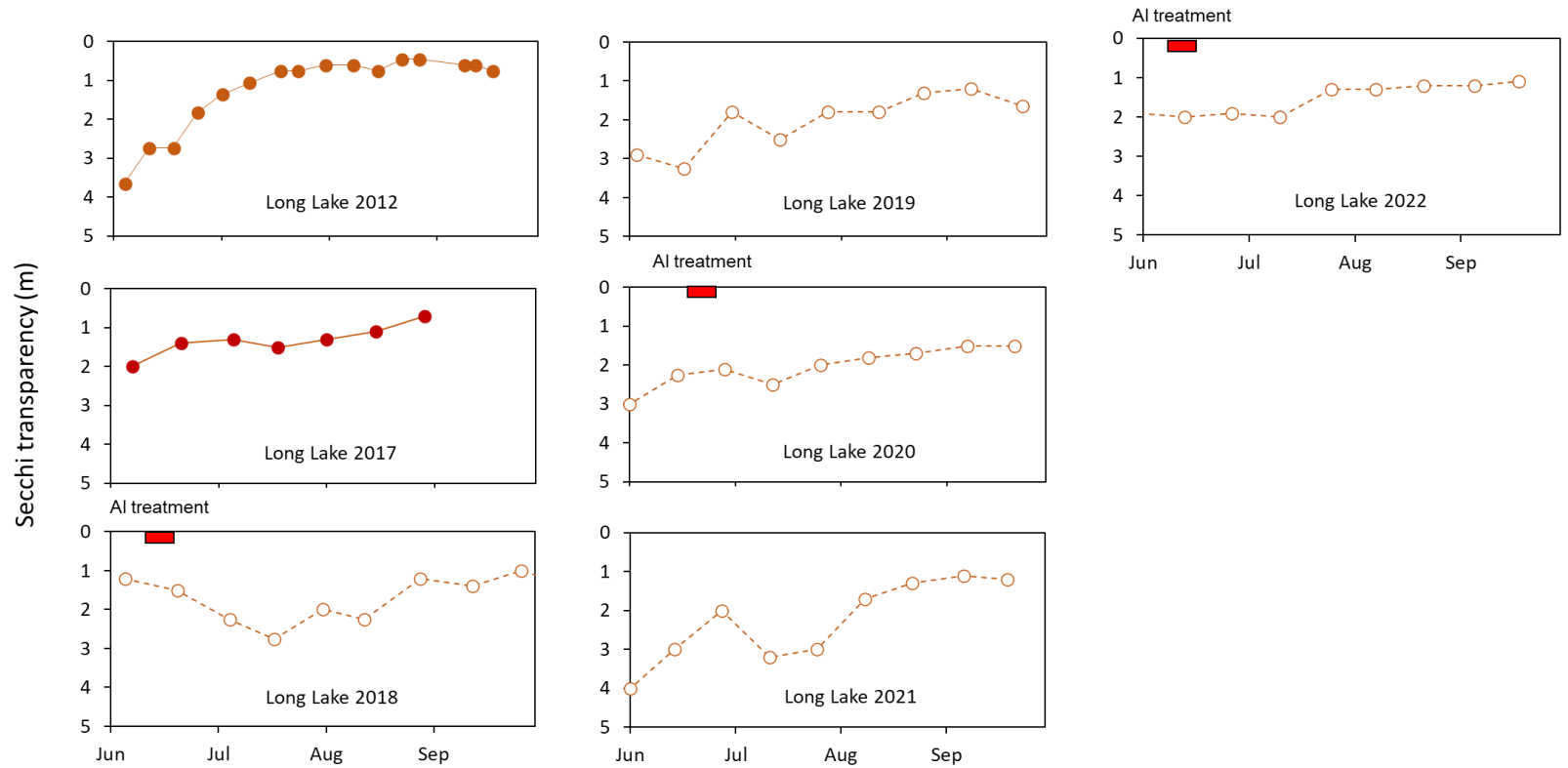
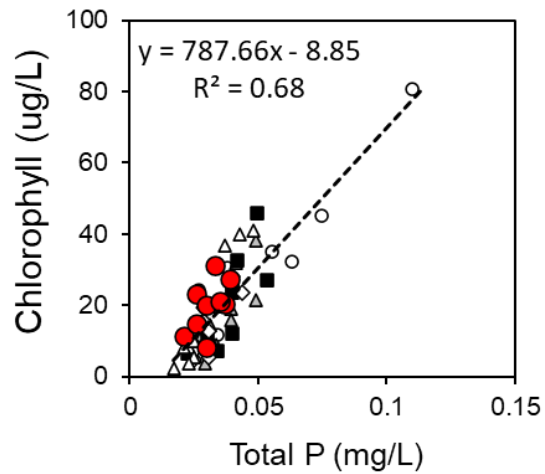
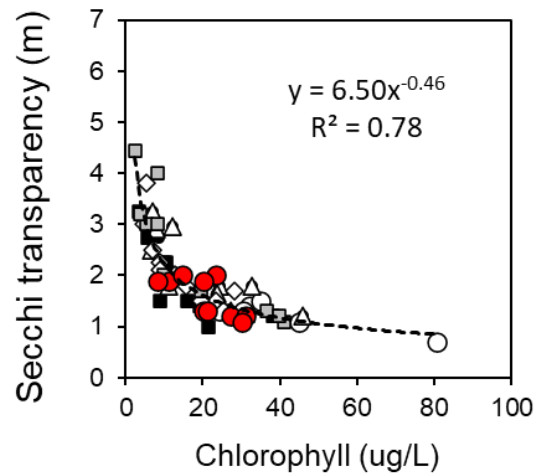


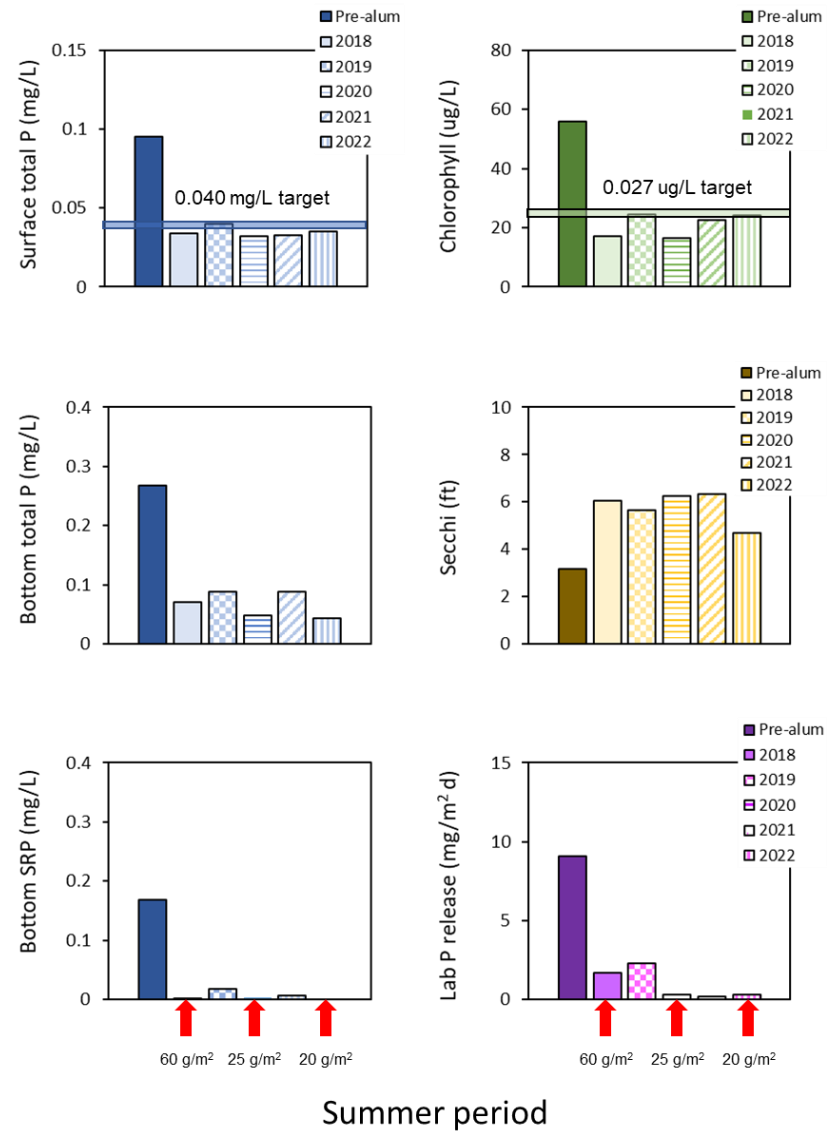
Figure 10. Seasonal variations in Secchi transparency during pretreatment (2012 & 2017) and post-treatment years. Red horizontal bars denote the periods of alum treatment.



- 2017
- 2018
- △ 2019
- ◇ 2020
- ◻ 2021
- 2022

Figure 11. Relationships between Secchi transparency and chlorophyll (upper panel) and total phosphorus (P) versus chlorophyll (lower panel) during the summer 2017 (pretreatment) and 2018-22 (post-treatment).

Figure 12. A comparison of mean summer (July-September) summer concentrations of surface and bottom total phosphorus (P) and soluble reactive P (SRP), chlorophyll, Secchi transparency, and mean laboratory-derived diffusive P flux from sediment (station 30) during pretreatment (2012 and 2017) and post alum treatment (2018-22) years. Red arrows denote alum treatment years.



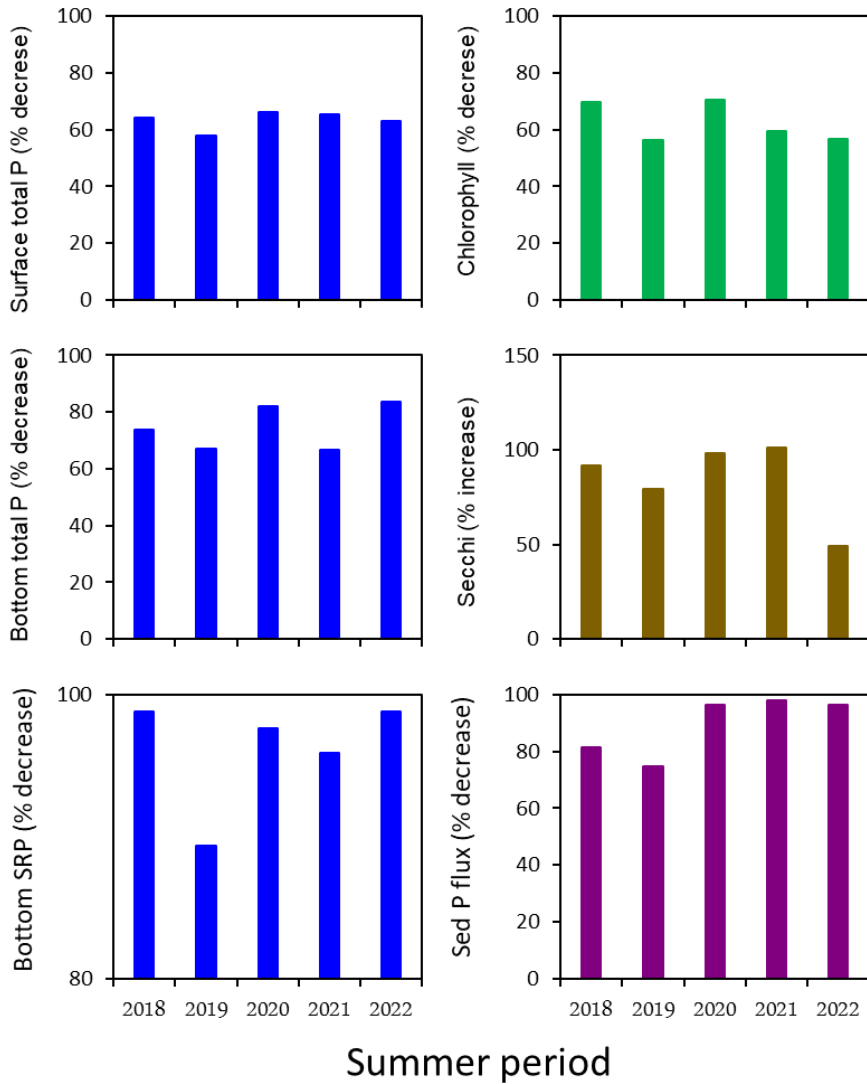
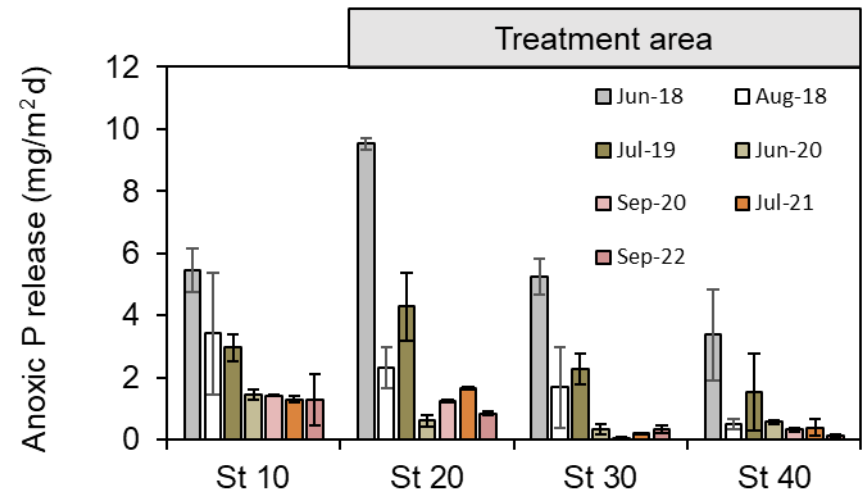


Figure 13. Summer (July-September) percent improvement in surface and bottom total phosphorus (P) and soluble reactive P (SRP), chlorophyll, Secchi transparency, and mean laboratory-derived diffusive P flux from sediment (station 30) during post alum treatment (2018-22) years.

Figure 14. A comparison of mean anaerobic phosphorus (P) release rates for various stations in Long Lake. Horizontal lines represent ± 1 standard error.



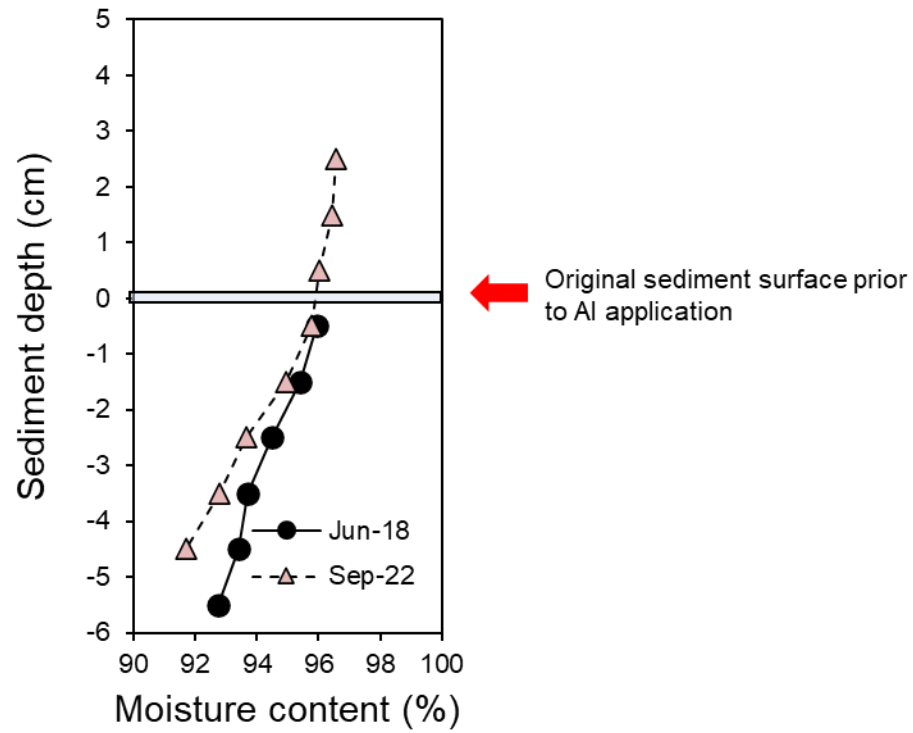


Figure 15. Vertical variations in sediment moisture content at station 30 (Figure 1) on June 2018 (immediately prior to the first Al application) and September 2022. The light blue horizontal line denotes the original sediment surface before Al applications. The Al floc settled on top of this interface and represents a new layer.

Figure 16. Variations in sediment total aluminum concentration in the upper 6-cm sediment layer in September 2022.

Figure 17. Variations in the areal aluminum concentration (g/m^2) in the upper 6-cm sediment within the alum treatment zone. The target Al application concentration after 3 treatments was 105 g/m^2 as denoted by the horizontal blue line.

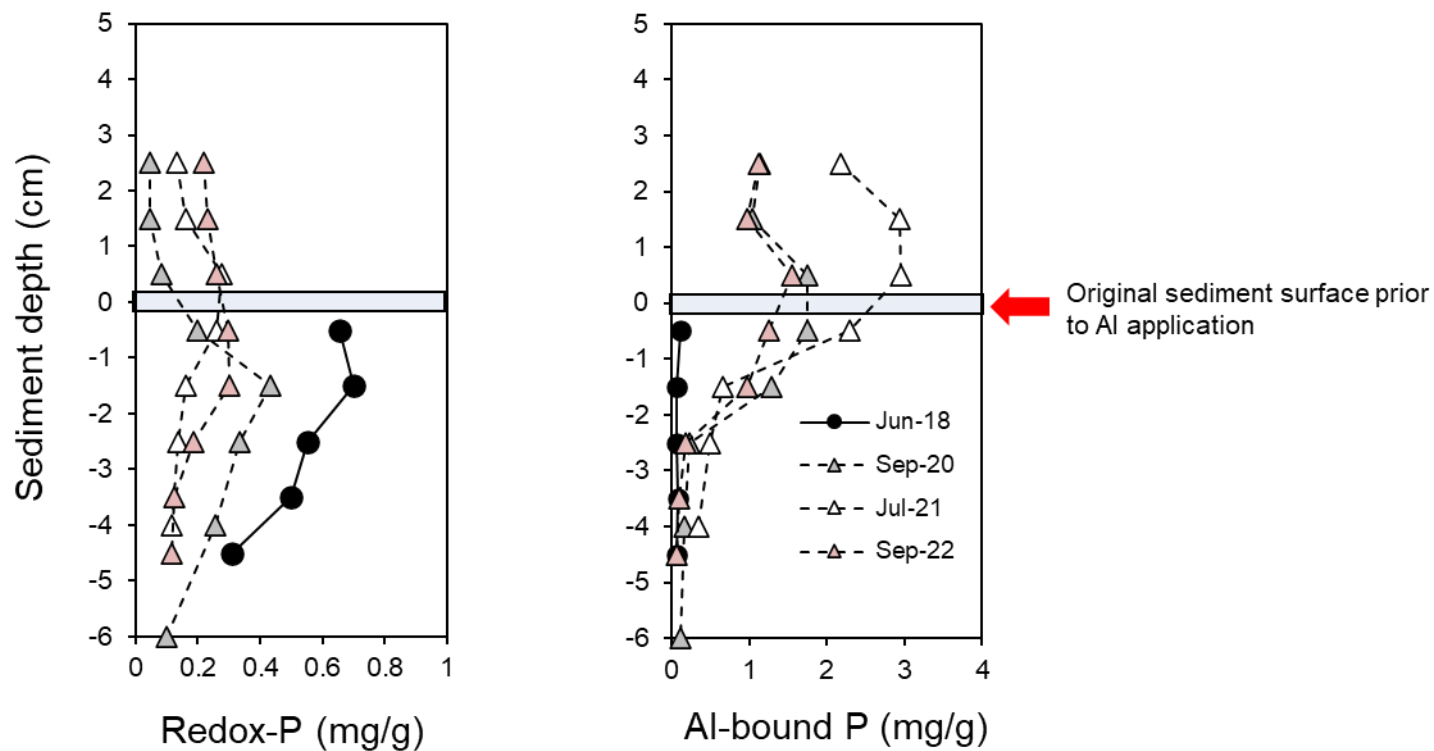


Figure 18. Vertical variations in sediment redox- (i.e., the sum of the loosely-bound P and iron-bound P sediment fractions) phosphorus (P) and aluminum (Al)-bound P concentrations for a sediment core collected from station 30 (Figure 1) in June 2018, September 2020 (after the 2nd Al treatment), July 2021, and September 2022 (after the 3rd Al treatment). The sediment profile in June represents pre-treatment conditions while 2020 - 2022 represent post-alum treatment conditions. The light blue horizontal line denotes the original sediment surface before Al applications. The Al floc settled on top of this interface and represents a new layer.